

REPORT DOCUMENTATION PAGE

Form Approved

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paper

AFRL-SR-AR-TR-03-

0443

ces,
this
rson

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE FINAL		3. REPL 01-APR-2001	
4. TITLE AND SUBTITLE A CHARACTERIZATION SYSTEM FOR CERAMIC POWDERS				5. FUNDING NUMBERS F49620-01-1-0260	
6. AUTHOR(S) I-WEI-CHEN					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF PENNSYLVANIA MATERIAL SCIENCE AND ENGINEERING 3231 WALNUT STREET, ROOM 424 LRSM PHILADELPHIA, PA 19104-6272				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 4015 WILSON BOULEVARD ARLINGTON, VA 22203				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release. Distribution is unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The grant was initiated on April 1, 2001. We have purchased a laser particle size analyzer, a powder surface area analyzer, a mercury powder pore size analyzer, and an ultracentrifuge for powder separation. These instruments have all been installed and in operation. We have proceeded with powder and green body characterization of the bulk silicon nitride and SiMON [®] s. This includes the study of the effect of seeding with micrometer-sized crystals on a-SiAlON microstructure, the development of ceramic cellular composites by green body deformation, and infiltration of C-N precursors into reaction bonded silicon nitride, and the development of a-SiAlON ceramics with machinability and low glass content.					
14. SUBJECT TERMS				15. NUMBER OF PAGES 7	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
20. LIMITATION OF ABSTRACT					

20031104 006

RECEIVED OCT 21 2003

I. TITLE OF PROJECT

A Characterization System for Ceramic Powders

FINAL REPORT

AUGUST 31, 2003

U.S. AIR FORCE GRANT NO. F49620-01-1-0260

PRINCIPAL INVESTIGATOR

I-WEI CHEN

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA

DISTRIBUTION STATEMENT A

Approved for Public Release
Distribution Unlimited

II. OBJECTIVES

We will develop a ceramic powder characterization system capable of measurement of particle size, pore size, surface area and their distributions to facilitate the research of structural ceramics and composites. Performance and processability of advanced ceramics and composites are critically dependent on the characteristics of starting powders and green bodies. These characteristics will be determined using the proposed system and further correlated to processing schedules, final microstructures, and mechanical properties. The equipment will benefit the ongoing research at the University of Pennsylvania on in-situ toughened α -SiAlON, O-SiAlON, reaction bonded silicon nitride, silicon oxynitride/carbonitride glasses, and micro-porous oxide/oxide composites that are of interest to the Air Force mission.

III. STATUS OF EFFORT

The grant was initiated on April 1, 2001. We have purchased a laser particle size analyzer, a powder surface area analyzer, a mercury powder pore size analyzer, and an ultracentrifuge for powder separation. These instruments have all been installed and in operation. We have proceeded with powder and green body characterization of the bulk silicon nitride and SiAlON's. This includes the study of the effect of seeding with micrometer-sized crystals on α -SiAlON microstructure, the development of ceramic cellular composites by green body deformation, and infiltration of C-N precursors into reaction bonded silicon nitride, and the development of α -SiAlON ceramics with machinability and low glass content.

IV. ACCOMPLISHMENTS/NEW FINDINGS

Microstructure Control of Seeded SiAlON Ceramics

Although anisotropic grain growth can in principle lead to microstructures containing elongated grains, this process may require very high processing temperatures. It may also lead to very large grains of a broad size distribution that are not optimal for mechanical performance. Therefore, a method for microstructure control in conjunction with anisotropic grain growth is desirable. This may be achieved by seeding with crystals that are sufficiently large to be more thermodynamically stable than the remaining grains. Preferred growth can then occur at these seeds which, in turn, consume the surrounding matrix. The microstructure thus obtained is much more uniform than unseeded ceramics and the process can often be achieved at a relatively low temperature. In ceramics which undergo a phase transformation during densification (i.e., reactive sintering), the driving force could be especially large for crystal nucleation, resulting in very small, equiaxed grains. This is the case of α -SiAlON and o-SiAlON, and for such ceramics seeding is especially advantageous. The complication here, however, is that the final ceramic has a phase and a composition that are both different from the starting materials. Therefore, the seed crystals not only need to be larger in size, but also be in equilibrium with the final ceramic; i.e., they should be of the same phase and composition.

We have developed a method for preparing seed crystals for a variety of α -SiAlON compositions. These ceramics have high hardness comparable to that of silicon carbide, and through microstructure control, high toughness comparable to that of conventional β -silicon nitride and β -SiAlON. To understand the microstructure development during

seeding, we have collected extensive statistics of grain geometry and dimensions. We found that seeds are generally stable regardless of shapes, and there is a one-to-one correspondence between seeds and final grains as long as coalescence is avoided. We have also measured the R-curves of the seeded ceramics to determine the optimal microstructure of the highest toughness. We found that in Y-containing α -SiAlON, the optimal fracture toughness, in excess of $10 \text{ MPa}\cdot\text{m}^{1/2}$, is obtained when 1 % small seeds were used. Strength and Weibull modulus have also been improved following the same trend of optimization. Ceramics with larger seeds reached the optimal toughness at the same number density of seeds, but at a higher volume % or weight %. In contrast, Ca-containing α -SiAlON seeded with crystals of a similar size reaches the optimal toughness at 8% seeding. This is because anisotropic grain growth in Ca-containing systems is more pronounced, resulting in very long grains that easily impinge each other. As a result, it is more difficult to obtain a microstructure in which a large portion is occupied by elongated grains. In Nd-containing α -SiAlON, the development is between the above two extremes of Y and Ca-SiAlON. These different ion effects on the kinetics and morphology can be understood in terms of ion segregation and interface kinetics.

The above approach is being extended to other α -SiAlONs and o-SiAlON, which has excellent oxidation resistance. A comparison of different rare earth oxide additives has identified the most beneficial composition for improving the fracture toughness and strength. A collaboration with Stevens Institute of Technology has identified the most beneficial composition for oxidation resistance, and confirmed that α -SiAlON has outstanding oxidation resistance compared to β -Si₃N₄. A collaboration with Oak Ridge National Laboratory has revealed the potential of using additives and seeding to tailor thermal expansion coefficients of α -SiAlON.

SiAlON/BN Composites

Hexagonal BN is known to have good corrosion resistance, thermal shock resistance and machinability, thus making it an excellent choice for incorporation in advanced nitride composites. Nano composites containing nanosized BN precursor that is converted during the sintering of silicon nitride have especially attractive properties. For example, the work on β -Si₃N₄/BN nanocomposites by Niihara et al. demonstrated machinable ceramics that retain 80% of the strength of monolithic silicon nitride, even at elevated temperature. We have developed a method for producing 99+% pure nanosized BN as well as nanocomposite powders of Si₃N₄/BN. These powders were used to prepare α -SiAlON/BN nanocomposite ceramics. The composite with 20 vol.% BN was machinable (could be drilled with WC-coated drill bit) and it retained up to 95% of the strength of monolithic α -SiAlON. Oxidation study showed an improvement in oxidation resistance over monolithic α -SiAlON material, with an up to 10-fold decrease in oxidation layer thickness after 24h annealing at 1000-1300 °C. Further study of microstructure control is under investigation.

Cellular Ceramic Composites

Ceramic layer composites have outstanding mechanical properties due to either an advantageous combination of the constituent properties or to the weak interface engineered into the layer structure. The major drawback, however, is on the processing

side because of the need of laminating in the green state, the relative poor sintering performance (delamination and shrinkage cracks), and the thickness restriction due to handling requirements. To circumvent these problems, we have recently developed a new method for fabricating ceramic laminates based on deformation processing (repeated rolling and folding) in the green state at room temperature. A surprising finding of this work is that novel cellular microstructures containing discontinuous layer phases can also be obtained by the same method. The initial work was performed using aqueous slurries. We have now demonstrated a similar approach using ceramic suspensions in paraffin-oil/paraffin which are more suitable for ceramics that are water sensitive.

The basis for microstructure control in this method is rested on the mechanical stability of bi-material interface. At large deformation, the interface becomes wavy unless the deformation resistance is identical across it. Such instability has previously been seen in metal rolling but is here applied to ceramic slurries. Deformation resistance of the slurry can be controlled by varying the composition of the carrier liquid. In the case of paraffin-oil/paraffin liquid, for example, the viscosity increases with the weight % of paraffin. A suitable formulation can then be found so that there is enough difference in the "hardness"/"softness" of the ceramic slurries, and the slurries are deformable at room temperature yet shape-retaining before and after deformation. Stacks of tapes can then be repeatedly rolled and folded to yield composites with layers as thin as several micrometers, with microstructures ranging from continuous, nearly planar layers to discontinuous, wavy layers.

Fired ceramics of alumina/zirconia composition have been found to have increasing strength as the layer thickness decreases. While the starting alumina ceramics have a strength of less than 300 MPa, the final strength of cellular ceramics with thin, interwoven layers have a strength exceeding 700 MPa. These composites have strong interfaces and the major strengthening mechanisms are attributed to transformation toughening and grain refinement.

A parallel series of zirconia/alumina composites with weak interface have also been developed using organic binders and plasticizers similar to those employed in conventional tape casting. Although this process requires warm pressing (around 100 °C), it again yields microstructures ranging from flat laminates to wavy, cellular composites. Weak interface was achieved in these ceramics by limiting the sintering density of the alumina layer, resulting in composites that fail (in bending) gracefully due to crack trapping and deflection at these layers.

Nucleation and Growth of β - Si_3N_4 / β -SiAlON Crystals from Liquid

The kinetics of nucleation and growth of β - Si_3N_4 / β -SiAlON crystals from liquid in the (Y,Mg)(Si,Al)(O,N) has been studied and surprising results have been obtained. We found, for the first time, definitive evidence of nucleation control by α - Si_3N_4 powders in the liquid, in contradiction to the conventional thinking on β - Si_3N_4 ceramics. This is the result of a very large supersaturation (at about 10 times the equilibrium concentration), which can be sustained in the glassy liquid but not in the ceramics. The coarsening kinetics was also found to be surprisingly robust, not showing the deceleration expected

for Oswald ripening. This is because of the concomitant conversion of β - Si_3N_4 to β -SiAlON, which provides an additional source of driving force that overwhelms the capillary driving force. The kinetics have been analytically modeled and found in good agreement with the observed particle size statistics.

Acknowledgement

This work was sponsored by the Air Force Office of Scientific Research, USAF, under the grant number F49620-01-1-0260. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

Research Personnel (None drawing salary from the present grant)

I-Wei Chen	Principal Investigator
Roman Shuba	PhD student
Misha Zenotch	Visiting research student

Publications

- (a) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "R-Curve Behavior of In-situ Toughened α -SiAlON Ceramics," *J. Am. Ceram. Soc.*, **84** [4] 884-86 (2001).
- (b) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "Synthesis of α -SiAlON Seed Crystals," *J. Am. Ceram. Soc.*, **84** [7] 1651-53 (2001).
- (c) I-W. Chen and E.J. Winn, "Delaminating Oxide Layered Composites with Wavy Interfaces," *Z. Metallk.*, **92**, 757-61 (2001).
- (d) I-Wei Chen and R. Shuba, "Structures and Properties of α -SiAlON Ceramics," in *Encyclopedia of Materials: Science and Technology*, Ed. K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilchner, E. J. Kramer and S. Mahajan, Elsevier Science, 2001, pp. 8471-76.
- (e) A. Pechenik and I-W. Chen, "Advanced Silicon Nitride Ceramics", *Advanced Materials and Processing*, p. 37, March (2001).
- (f) I-W. Chen, E.J. Winn and M. Menon, "Application of Deformation Instability to Microstructural Control in Multilayer Ceramic Composites," *Mater. Sci. Eng.*, **A317**, 226-35 (2001).
- (g) M. Schwarz, A. Zerr, E. Kroke, G. Miehe, I-W. Chen, M. Heck, B. Thybusch, B. Toe, and R. Riedel, "Spinel Sialons," *Angew. Chem. Int. Ed.* **41** [5]. 789-93 (2002).
- (h) A. Dakskobler, T. Kosmac and I-W. Chen, "Paraffin-based Process for Processing Layered Composites with Cellular Microstructures," *J. Am. Ceram. Soc.*, **85** [4], 1013-15 (2002).
- (i) M. Zenotchkine, R. Shuba, J-S. Kim and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α -SiAlON: I. Y-SiAlON," *J. Am. Ceram. Soc.*, **85** [5] 1254-59 (2002).
- (j) M. Zenotchkine, R. Shuba, J-S. Kim and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α -SiAlON: II. Ca-SiAlON," *J. Am. Ceram. Soc.*, **85** [5] 1260-67 (2002).

- (k) M. Zenotchkine, R. Shuba, and I-W. Chen, "Effect of Heating Schedule on the Microstructure and Fracture Toughness of α -SiAlON: Cause and Solution," *J. Am. Ceram. Soc.*, **85** [7] 1882-84 (2002).
- (l) I-W. Chen, L. Wang and A. Davenport, "Accelerated Precipitate Coarsening due to a Concomitant Secondary Phase Transformation," *Acta Materialia*, **51** [6] 1691 - 1703 (2003).
- (m) M. Zenotchkine, R. Shuba, and I-W. Chen, "Effect of Seeding on the Microstructure and Mechanical Properties of α -SiAlON: III. Comparison of Modifying Cations," *J. Am. Ceram. Soc.* **86** [7] 1168-75 (2003).
- (n) L. Wang, T-Y. Tien, and I-W. Chen, "Formation of Beta Silicon Nitride Crystals from (Si,Al,Mg,Y)-(O,N) Liquid--I. Phase, Composition and Shape Evolutions," *J. Am. Ceram. Soc.* **86** [9] 1578-85 (2003).
- (o) L. Wang, T-Y. Tien, and I-W. Chen, "Formation of Beta Silicon Nitride Crystals from (Si,Al,Mg,Y)-(O,N) Liquid-- II. Population Dynamics and Coarsening Kinetics," *J. Am. Ceram. Soc.* **86** [9] 1586-91 (2003).

TRANSITIONS/PATENTS

Samples of *in-situ* toughened α -SiAlON have been provided to several US manufacturing and engineering concerns to evaluate their performance. This evaluation process is ongoing as the performance is application specific, depending on the condition, environment and material system. Thus, composition, microstructure and property optimization is required for each application.

Samples of *in-situ* toughened α -SiAlON have been provided to Dr. Paul Becher of Oak Ridge National Laboratory to evaluate the thermal expansion coefficients. A large effect of dopants and seeding has been found, which makes it possible to tailor the ceramics to have different thermal expansion behavior. A preliminary report to Department of Energy has been submitted to document these results. (Not cited here.)

Collaborative research with Prof. R. Riedel of Damstadt Technical University of Germany has resulted in the discovery of a new structure of solid solution of Si-Al-O-N. A patent application has been filed with Prof. Chen as a co-inventor.

Collaborative research with Prof. H. Du of Stevens Institute of Technology has been initiated to investigate the oxidation resistance of α -Sialon. Certain compositions are found to perform favorably compared to the state-of-the-art commercial β -Si₃N₄. A manuscript has been prepared to report the first results. (Not cited above.)

The PI gave a Keynote lecture, "Development of Tough α -SIALON," in the International Symposium on SIALONS, Chiba, Japan, December 2001.

The PI gave an invited talk, "Microstructure Development in Silicon Nitride-Issues and Plausible Resolutions," in the annual meeting of the American Ceramic Society, St. Louis, April-May 2002.

The PI gave an invited lecture, "Recent Advances in Tough α -SIALON," in the Annual Meeting of the American Ceramic Society, Centennial Celebration Symposium of First Flight, Nashville, May 2003.

Forthcoming invited talks are at Composite Symposium at Lake Louise, Canada in October, 2003, Advanced Ceramics Workshop at Atami, Japan in November, 2003, and Silicon Based Structural Ceramics Meeting at Seoul, Korea in June, 2004.